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THE DETERMINATION OF PYRITIC SULPHUR IN COAL BY ATOMIC ABSORPTION - A NEW APPROACH

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The Determination of Pyritic Sulphur in Coal
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by

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INTRODUCTION

Modern analytical methods for the determination of the forms of sulphur in coal are based on the work of A.R. Powell (1921). After considerable experimentation Powell concluded that sulphur in the sulphate form, and iron in the non-pyritic form is soluble in dilute hydrochloric acid, whereas pyrite is insoluble under the same conditions. On the basis of this evidence it is logical to conclude that the only iron remaining after dissolution in hydrochloric acid is that associated with the pyrite. If the coal remaining after the hydrochloric acid extraction is then ashed, and the iron determined directly by either titration or atomic absorption, the pyrite could then be calculated, using the gravimetric factor 1.148, i.e. S_2/Fe .

1. Summary of Method

- 1.1 Pyritic sulphur is determined on the residue remaining after extraction with dilute hydrochloric acid, as described in ASTM D 2492. The extracted coal is ashed to constant weight, fused with lithium tetraborate, dissolved in hydrochloric acid and the iron determined by atomic absorption.

2. Procedure

- 2.1 Weigh to the nearest 0.1 mg, 1 g of air dried laboratory sample crushed to pass a No 60 (250 μm) sieve, and transfer to a 250 ml Erlenmeyer flask, and add 20 ml HCl (2:3). Shake the flask until the coal is thoroughly wetted, and then add an additional 30 ml HCl (2:3) to wash down any coal adhering to the sides of the flask. Fit a cold finger

condenser into the neck of the flask and boil on a hot plate under reflux conditions for 60 minutes, then rinse the cold finger condenser with HCl (1:23) and filter through a medium textured, double acid-washed filter paper into a 400 ml beaker. Transfer the residue to the filter and wash six times with HCl (1:23) using a total volume of about 35 ml. Transfer the filter paper and contained residue to a 35 ml platinum crucible. Place the crucible in a cold muffle furnace and ignite to constant weight at $750 \pm 10^{\circ}\text{C}$; at least 2 hours are required.

- 2.2 The crucible is then removed, cooled, and 0.5 g of lithium tetraborate added. The ash and lithium tetraborate are well mixed, and then covered with an additional 0.5 g of lithium tetraborate. Place the crucible in a clean silica or refractory tray and introduce into a muffle furnace preheated to 1000°C . Fifteen minutes at this temperature is usually sufficient to fuse the mixture completely. Remove the tray and crucible and allow to cool to room temperature. Carefully rinse the bottom of the crucible with distilled water to remove any possible contamination, and then place in a 250 ml beaker. Place a teflon coated stirring bar inside the crucible and add 150 ml of 5% hydrochloric acid, and place on a stirring hot plate. Bring to just below boiling and maintain for 30 minutes with constant stirring.
- 2.3 Remove the beaker from the hotplate and allow to cool to room temperature. Quantitatively transfer the solution to a 200 ml volumetric flask, wash beaker and crucible with HCl (5%) and bring to the mark with HCl (5%).

3. Determination of Iron by Atomic Absorption

3.1 Sample Solution Aliquot

To a 100 ml volumetric flask add a 10 ml aliquot of the sample solution and 10 ml of lanthanum chloride solution (10%), and bring to the mark with HCl (5%).

4. Standard Preparation

4.1 To a 100 ml volumetric flask add an aliquot from the 1000 ppm iron stock solution, and 10 ml of lanthanum chloride solution (10%) and bring to the mark with HCl (5%). The size of the aliquot taken will depend on the expected concentration of iron in the sample.

4.2 Program the instrument as recommended by the instrument manufacturer and run standards and samples. Record iron content in ppm.

4.3 Calculations

$$\% \text{ Pyritic S} = \frac{F \times A \times D \times 100 \times 1.148}{C_s}$$

where:

F = correction factor for amount of ash used $F = \frac{\text{Wt ash obtained}}{\text{Wt ash used}}$

A = ppm Fe

D = dilution factor

C_s = ppm Fe in sample solution

$$\left(\frac{\text{Wt sample (mg)}}{\text{Vol of Soln (l)}} \right)$$

1.148 = gravimetric factor S_2/Fe

NOTE

Alternatively the determination of iron may be carried out on the residue from the HCl extraction of the sulphate sulphur as described in ASTM D 2492. This residue may be ashed and if the weight of ash is too great a portion may be used. The ash should then be ground to pass a No.200 (74 μm) sieve and reignedited at 750°C.

A 0.2 g sample of the ash is then analysed as described above.

5. As an alternate to the lithium tetraborate fusion technique

2.2 the ashed sample may be dissolved in hydrochloric acid prior to the determination of iron by atomic absorption as follows:

5.1 The cooled crucible from 2.1 is placed in a 400 ml beaker, with a teflon coated stirring bar. Add 150 ml of HCl 2:3 and place on a stirring hot-plate. Bring to just below boiling and maintain for 1 hour with constant stirring. Determine the iron as described in the fusion technique.

6. Analytical Results

6.1 Nine samples, covering a wide range of sulphur values were analysed by the method described in ASTM D 2492 and by the method described above. The determined values by the two methods appear in Table I

TABLE I					
D-2492					
E.R.L. No.	% Total S	% Sulphate S	% Organic S	% Pyritic S	Modified A/A % Pyritic S. Dif.
2661-76	1.75	0.06	1.07	0.62	0.66 + 0.04
2639-76	8.50	0.12	0.53	7.85	7.80 - 0.05
2676-76	4.45	0.24	1.81	2.40	2.10 - 0.30
2147-78	1.70	0.06	0.92	0.72	0.74 + 0.02
2148-78	4.69	0.22	2.39	2.08	2.18 + 0.10
2149-78	0.38	0.06	0.23	0.09	0.06 - 0.03
2678-76	3.15	0.09	1.59	1.47	1.68 + 0.21
2680-76	9.19	0.26	1.97	6.96	6.94 - 0.02
2642-76	4.23	0.04	1.16	3.03	3.21 + 0.19

Repeatability ASTM D 2492

Sulphate sulphur	0.02%
Pyritic sulphur under 2%	0.05%
Pyritic sulphur over 2%	0.10%

Reproducibility

Sulphate sulphur	0.04
Pyritic sulphur under 2%	0.30
Pyritic sulphur over 2%	0.40